Computer simulations of epoxy binding on iron oxide surfaces

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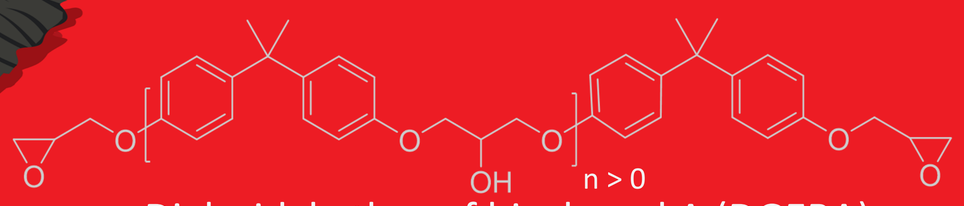
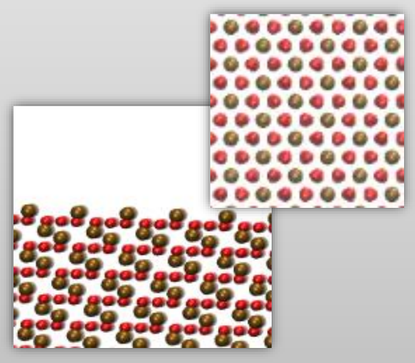
Epoxy resins have a wide range of applications as polymer adhesives and protective coatings, from aerospace and marine applications through to nontoxic interior coatings in the food industry [1]. In all cases, the performance of the final solid-polymer system is dependent on the physicochemical properties of the interface and the interaction between the polymer and the solid substrate. However, experimental methods to characterize this interaction are limited and mostly deteriorative to the interface. We perform molecular dynamics simulations to calculate the binding energy ($\Delta E_{binding}$) given by:

Binding Energy = Energy of adsorbate on surface − [Energy of adsorbate + Energy of Surface]



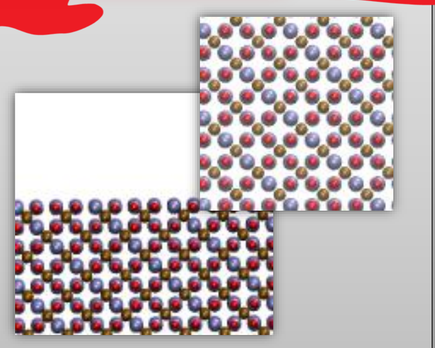
Diglycidyl ether of bisphenol A (DGEBA)

The adsorbate (DGEBA) is modelled using OPLS-AA [2]. We investigate n = 0,1,2,3



Hematite, Fe_2O_3 (0001) surface

The iron oxide surfaces investigated are modelled with CLAYFF [3]. We look at pristine hematite (Fe_2O_3) and magnetite (Fe_3O_4) surfaces. To investigate this, we vary the fraction of surface iron functionalised with a hydroxyl group from 0 (pristine) to 1 (all possible iron sites are functionalised). All simulations are done at 300K.

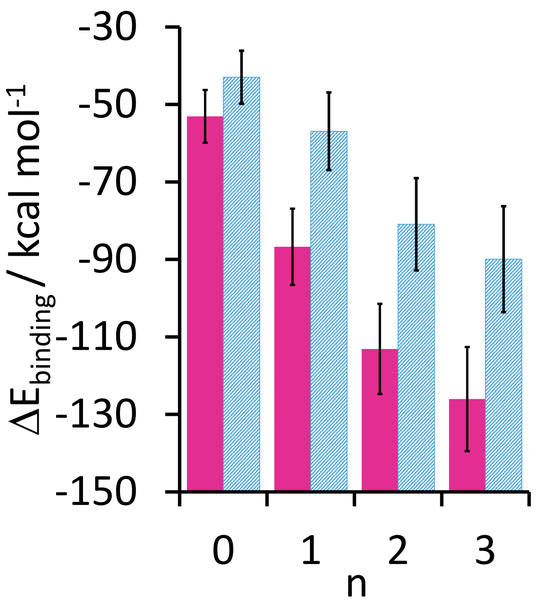


Magnetite, Fe_3O_4 (100) surface

● = Oxygen, Charge = -1.050 ● = Fe(Tet), Charge = +1.575 ● = Fe(Oct), Charge = +1.3125

Adsorbate Length

The dominant interaction is between the oxygen in the DGEBA and the iron on the surface.

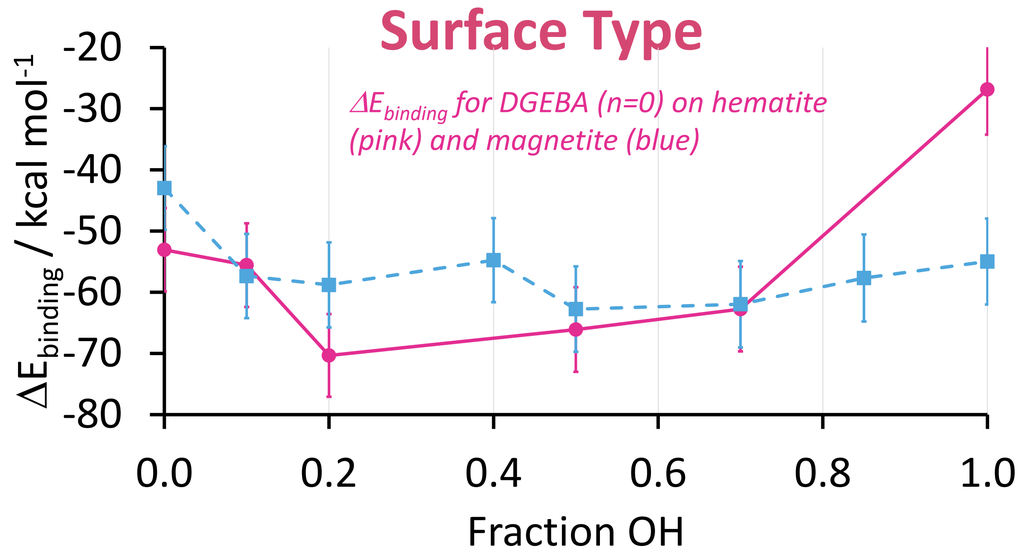


$\Delta E_{binding}$ for DGEBA on pristine (no OH) hematite (pink) and magnetite (blue)

As n increases the number of Fe-O interactions increases and $\Delta E_{binding}$ becomes more favourable.

However, as n increases, the molecules become more flexible and not all O can reach the surface, meaning as the DGEBA gets longer each additional repeat unit contributes less to the $\Delta E_{binding}$

Surface Type



A small fraction of OH increases the binding strength for both hematite and magnetite. However, a large OH fraction for hematite block any Fe-O interactions and causes $\Delta E_{binding}$ to become less favourable. This is not seen for magnetite as the surface still has uncovered iron sites available.

Conclusions and future work

- Fe (surface) – O (adsorbate) interactions dominate the $\Delta E_{binding}$
- DGEBA bonds preferentially to pristine hematite, but when fully hydroxylated binds more strongly to magnetite
- Future work will look at the free energy contributions and the role of entropy on surface binding

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